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Study on Gas Sensor of Hybrid Organic Molecule and Sensitive Properties of Toxic Gas

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Abstract

According to the low power and the chemical modifiction properties of organic gas-sensing material, the organic semiconductor material of molecule hybrid CuPc and PANI was used as gas-sensing film, and the gas sensor which has high selectivity to toxic gas was investigated. CuPc was synthesized with Phthalonitrile and p-Cresol as the source material of benzene ring by the template synthesis method of two steps reaction. Through doping with perchloric acid, vitriol and nitric acid, semiconducting doped PANI was obtained. By means of molecular hybrid modification, the intermediate substance of CuPc and PANI was polymerized and formed a kind of new organic semiconductor material CuPcxPANI1-x. Sensor chip was made by virtue of semiconductor technology; the combination of chip and new sensitive material was achieved by virtue of vacuum coating technology. The film surface morphology were characterized through SEM, and it showed that the sensitive material was made of rounded particles whose diameter was about 200nm; the surface of film was deposited by odontoid particals, whose diameter is 200nm or so, and relatively uniform, and its aperture is ordered. The gas sensing properties of thin film were tested by static volumetric method. The results indicate that the new organic semiconductor hybrid material is sensitive to the toxic gases of sulfur dioxide, nitride dioxide, chlorine ect.; the selectivity can be improved by changing the ratio of the distribution; When the heating voltage is 1.5V, the output resistance can be stabilized within 5% and the sensitivity within 10% in 6 months.

Keywords-:organic molecule, hybrid, gas sensor, sensitive properties

1. Introduction

Material MPc, which has the conjugated macrocyclic structure, is a kind of organic gas sensitive material which has application foreground [1-2]. Below normal temperature, it has high sensitivity and selectivity, good heat resistance, acid resistance, alkali resistance and bright color, etc.. But the solubility of pure MPc is very poor in organic solvent. This causes the producing technique of equipment and material

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is complicated and limits its practical application at a great extent. The solubility of pure MPc can be changed, if using soft chain to modify macrocyclic periphery of molecule[3].

Phthalocyanin was synthesized according to the template synthesis method of reference[4]. Polyaniline was synthesized according to the chemical oxygenation synthesis method in reference[5]. CuPc was synthesized with phthalonitrile and p-Cresol as the source material of benzene ring by the template synthesis method of two steps reaction; through changed the composition of CuPc, PANI was used to modify CuPc by the techinique of molecule hybrid and new gas sensitive material hybrided by two kinds of organic material was obtained. Gas sensor was made and gas sensative property was analized.

2. Experiment

2.1 Reagents and Equipments

P-Cresol,4-Nitrophthalonitrile, 1,8-diazabicyclo[5.4.0] undec-7-ene(DBU), N,N-Dimethylformamide (DMF), Cupric chloride, amyl alcohol, Ammonium persulfate, Aminobenzene, etc..(reagents above are all analytical pure.)

JH-04 laser scribing machine; JGP560C Magnetic Enhanced Sputter; H52-10 Spin Coater; SB-401B double exposure machine; DM-450C vacuum plating machine (vacuum degree 0.62 Pa, evaporing current 10-20A); FEI sirion200 electron scan microscope(SEM) (Holland, Company Philips).

2.2 Sensor production

According to the reference[6], coppe phthalocyanine was synthesized with 4-Nitrophthalonitrile and p-Cresol as the source material of benzene ring by the template synthesis method; polyaniline was synthesized with aminobenzene as the source material of benzene ring by the chemical oxygenation synthesis method and then semiconducting doped PANI was obtained by doping with perchloric acid, vitriol and nitric acid. On the basis of synthesizing method of two materials above, by means of molecular hybrid modification, CuPc and PANI was polymerized and formed a kind of new organic semiconductor material $CuPc_xPANI_{1-x.}$

Underlaying material of sensor chip was ceramic substrate $AlB_{2B}OB_{3B}$ (film thickness 200nm) made by the technique of electrochemistry growth. Interdigital electrode was made by the microprocessing technology of laser scribing machine, and then sensitive material was vapordeposited on the electrode(Fig.1).

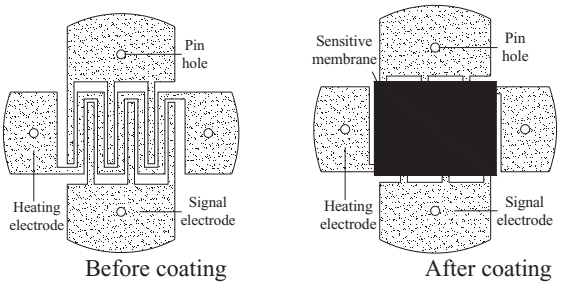

Fig.1 Scheme of planar structure of interdigital electrodes

The picture manufacturing process of sensor chip: clean the substrate and sputter film Pt on the surface of the polished substrate through Magnetic Enhanced Sputter; galatinize with Spin Coater and exposure through the double exposure machine and develop(etc.). And then, the picture of heater and lower electrode were formed by backwashing erosion.

The manufacturing process of the sensitive films: vapor-deposite gas sensitive material on the surface of a pair of lower electrode by means of vacuum evaporation, and vacuum drying hybrid for an hour at the temperature of 120℃. And then get film Au (0.01-0.1mg) and vacuum plate Au (within 10s) to form electrode on the surface of sensitive film by using of phase mask.

2.3 Testy of gas sensitive property

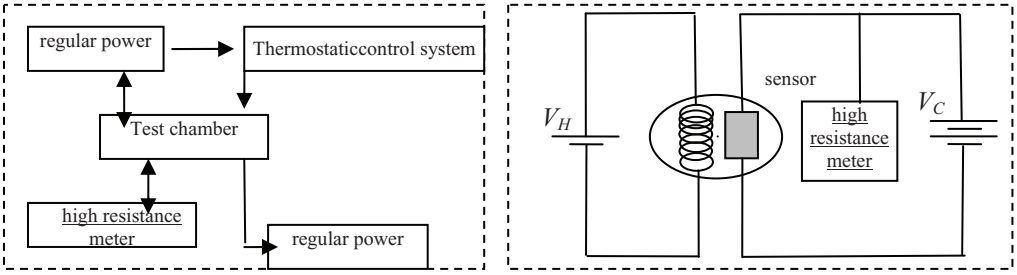

Fig.2 Test circuit and test system of semiconductor poison gas sensor

Fig.2 is the testing system and circuit of semiconductor toxic sensor. The testing conditions: heating voltage V_H is tunable from 0V to 15V; loop voltage V_C is 10V; test the gas sensitive properties of toxic gas Cl_2, SO_2, NO_2 separately by the static method. crystallizated with distilled water and acetone, Vacuum dried to get the sensitive material, CuPcxPANI1-x.

3. Results and discussion

3.1 SEM analysis of surface of the film

Fig.3 is SEM surface topography of platitum film at the condition of different sputtering power. It shows that thin film is ranked densely with tiny grain when sputtering power is 28.8W. The surface of film is level and its fluctuation is small(Fig.3a). While sputtering power is 37.4W, the quality of thin film begins to drop, grain begins to be rough, and fluctuation gets bigger(Fig.3b). The grain dimension of surface of the thin film gets much bigger, surface roughness increases, and quality of surface turns bad, when sputtering power is 54W(Fig.3c).

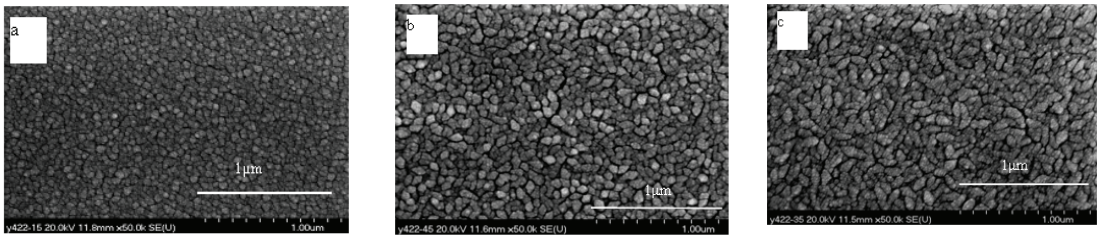

Fig. 3 Surface of Pt film by SEM under different sputtering powesr (Sputtering power/ W: a: 28.8, b: 37.4; c: 54)

Fig.4 is the scanning electron microscope picture of film fracture at the sputtering time of two miniutes when sputtering power is 28.8W. It shows that film is very thin and asymmetrical, and some areas even havn't been covered completely because sputtering time is short. So the coating time can't be too short.

Fig.5 is the SEM picture of the coated $CuPc_xPANI_{1-x}$ at different evaporing condition. When evaporing temperature was about 200℃（a）and 350℃（b）, the surface of film showed a kind of depositing growth partical like tooth whose diameter was about 200nm, relatively uniform and its aperture was ordered. Consequently, the gas sensitive properties of sensor producted at this condition is most evident; When the evaporing temperature is very high(about 650℃~750℃), although $CuPc_xPANI_{1-x}$ isn't decomposited, "favoid" structure which has more active is formed; mixture tends to carbonize, and the sensor loses the semiconducting properties.

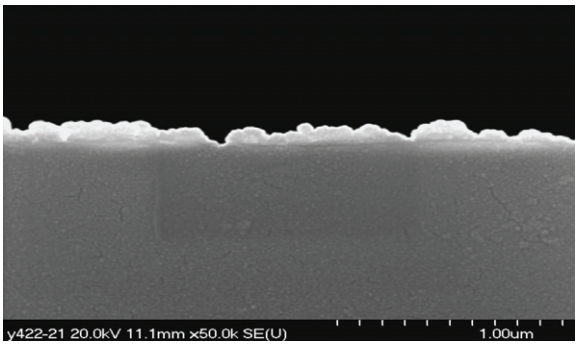

Fig.4 Fracture surface of the Pt film by SEM

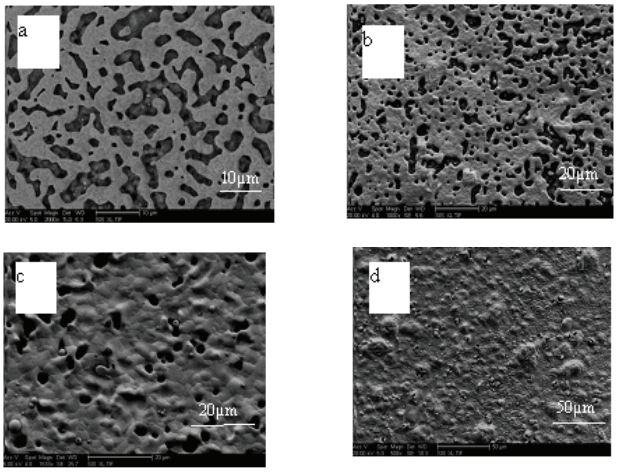

Fig.5 SEM of $CuPc_xPANI_{1-x}$ under different evaporation condition
Evaporation temp/℃: a: 200; b: 350; c: 650; d: 750

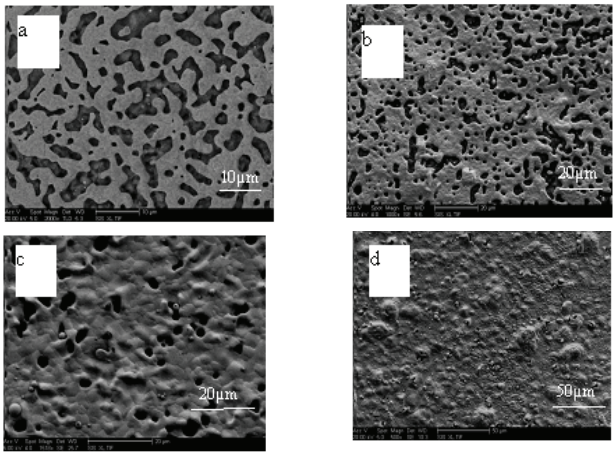

Fig.6 SEM microstructure of porous up-electrode under different evaporation
evaporation of up-electrode/s: a: 8s; b: 12 s; c: 13 s; d: 18 s

Fig.6 is the SEM microtopography of polyporous top electrode at the different evaporing conditions (vaporing current is 100~120A, vaporing time is 8~18s). Experiments indicate that when vaporing time is 8~12s, filmed polyporous top electrode emerges continuous and polyporous surface state, and ensures the conductible and ventilated properties..

3.2 Study on microprocess

Fig.7 is the relationship between devilling depth and width of Al_2O_3 ceramic substrate and impulse frequency of laser process. When laser Q frequency increases gradually, devilling depth increases but its tendency decreases. When laser Q frequency reaches a certain value (about 8kHz), if laser Q frequency keeps increasing , the devilling depth will decrease gradually. After the laser Q frequency passes 15kHz, the devilling depth will not be affected almostly by the laser Q frequency. With the increase of laser Q frequency, the energy gets more concentrated, and devilling width begins to be narrow slowly. When Q frequency keeps increasing, the average output power of laser will increase and the influenced area will enlarge. Thus the devilling width enlarges. When the influenced area is minimal, Q frequency is about 9kHz.

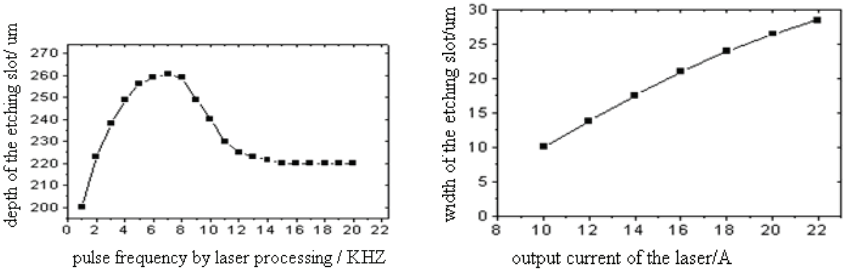

Fig. 7 Relation between the pulse frequency by laser processing and depth, width of the etching slot

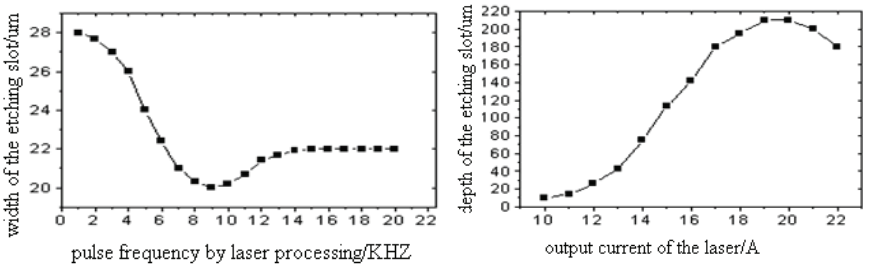

Fig. 8 Relation between output current of the laser and depth, width of the etching slot

Fig.8 is the relationship between devilling depth and width of Al_2O_3 ceramic substrate and output current of laser processing. If the range of current outputed by laser is 8~22A, devilling depth and width will increase as current rising. This is because laser energy absorbed by sample material at unit time increases, as laser output current rising.

3.3 Analysis of gas sensitive properties

Fig.9 is the sensibility curve of MPc_xPANI_{1-x} under the different heater voltage when the ratio is optimal. The experimental data shows that proper heater voltage (V_H), which is 1~2.5V (equivalent to 50℃~120℃), can improve the sensitivity characteristics and response-recovery properties. But when V_H is more than 2.5 V, because the absorption activity of the sensitive material tends to be saturated when temperature rises, it is meaningless to enhance sensitivity. So, it is ideal comparetively to choose the V_H of 1.5V.

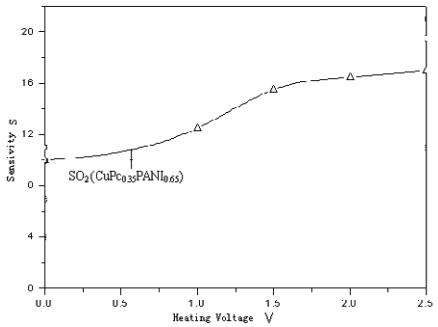

Fig. 9 Sensitivity curve of MPc_xPANI_{1-x} under the differen

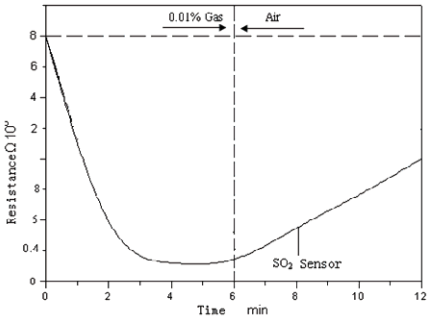

Fig.10 Responsive recovery curve of MPc_xPANI_{1-x} when heated at 1.5 voltages with optimal proportionality t heating voltage

Fig.10 is response-recovery curve of MPc_xPANI_{1-x} under 1.5V heater voltage when the ratio is optimal. The change rate of resistance can be over 67% within 30s. If recovery time is a little longer, it can still be over 67% of original value within 4 minutes. But through observed for a long time, sensor is hard to recover to the original value, and decrease of resistance is always 0.05~0.1%. It is probably because gas sensitive theory is a kind of chemical absorption and there are always a spot of gas molecules which are difficult to escape linkage action of sensitive film. Thermodynamic energy needed by desorption diffusion tends to decrease and this can be considered as the internal cause which results in the aging failure of the sensor.

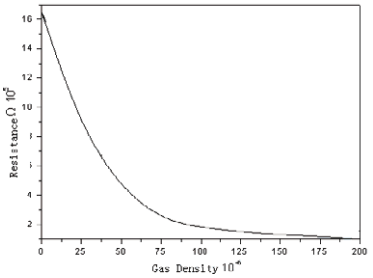

Fig.11 The relation curve between sensor resistance and gas concentration.

Fig.11 is the relation curve between sensor resistance and gas concentration. The results show: When gas concentration is below 50×10^{-6}, the rate of output impedance of sensor is very large, and the

relationship of saith and logarithm is not quite obvious. When the range is （50~125）$\times 10^{-6}$, the relationship of saith and logarithm is obvious. While the gas concentration is over 150×10^{-6}, the ratio of output resistance is very small, tends to be stable and be up to the testing toplimit. It also shows that the effective sensitive space of the organic semiconducting film is smaller than that of the inorganic semiconducting film. Consequently, the gas testing range of sensor is between 0 and 200×10^{-6}. This range is enough to test the toxic gas (generally, the test toplimit of the toxic gas is about 100×10^{-6}).

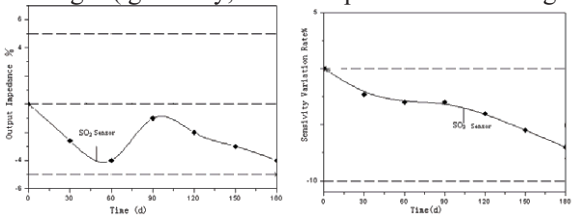

Fig.12 Stability carve of the sensor output impedance and sensitivity in six months

Fig.12 is the stability curve of sensor in six months. Output resistance ratio=$(R'-R)/R$. Sensitivity ratio = $(S'-S)/S$ (R' — present output resistance; R— initial output resistance; S' — present sensitivity; S— initial sensitivity)

The picture shows: output resistance of sensor fluctuates around the initial value; the total trendency drops down; sensitivity tends to be small; within six months, output resistance of sensor in the air decreases by less than 5%, and sensitivity decreases by less than 10%.

4. Conclusion

CuPc was synthesized with Phthalonitrile and p-Cresol as the source material of benzene ring by the template synthesis method. Through doping with perchloric acid, vitriol and nitric acid, semiconducting doped PANI was obtained. By means of molecular hybrid modification, CuPc and PANI was polymerized and formed a kind of new organic semiconductor material $CuPc_xPANI_{1-x.}$ Thin film was ranked densely with tiny grain when sputtering power was 28.8W. The surface of film was level and its fluctuation was small; sputtering time couldn't be less than two minutes. When evaporing temperature of process of sensitive film was 200℃~ 350℃, the surface of film showed active state of deposition growth of partical. The diameter of the particle was uniform and its aperture was ordered. At this time, the particle had bigger specific surface area, and gas sensitivity of sensor was the most obvious. Therefore, the best evaporing condition of polyporous top electrode is that vaporing current is 100~120A and vaporing time is 8~12s. When impulse Q frequency of laser processing is 9kHz, and laser output current is controled between 10A and 20A, the devilling depth and width is the best. If the heating voltage V_H is 1~2.5V (equivalent to 50℃~120℃), the sensitivity, response and resume property will be improved. The testing range of sensor which tests the gases such as SO_2, NO_2, Cl_2, is between 0 and 200×10^{-6}, V_H is 1.5V; output resistance can be stabilized within 5% and the sensitivity within 10% in 6 months. But through observed for a long time, sensor is hard to resume to the original value, and the decrease of resistance is always 0.05~0.1%.

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References

[1] Zuo Xia, Wei Yong-De, Wu Yi-Qun. High Sensitive and Selective Gas Sensing Materials Metallophthalocyanines[J]. Progess in Chemistry, 2004, 16(1): 68

[2] Eranna G, Joshi B C, Runthala D P. Critical Review in Solid State and Materials Sciences[J]. 2004, 29(3－4): 111

[3] MA Li, FENG Li-Jun, GAN Meng-Yu, et al. Synthesis and Properties of Conducting Polyaniline Doped with Multiple Sulfonic Acid[J].Chinese J Appl Chem, 2008, 25(2): 142

[4] Yuan S. Feng, Chen Z. Rong. Journal of Physical Chemistry A[J], 2005, 109 (11): 2582

[5] Rao Palle Swapna, Sathyanarayana D.N., Palaniappan S..Macromolecules[J], 2002, 35 (13): 4988

[6] Shi Yunfen, Shi Yunbo, Wang Liquan, et al. Preparation and Gas Sensitive Properties of PANI /CuPc Organic Semiconductor Hybrid Material[J]. Journal of Lanzhou University. 2009, 45(3): 86-91